

Chapter 3

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PHYSICAL PROPERTIES OF SOYBEAN OIL

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INTRODUCTION

Reports on the physical properties of soybean oil are relatively few and mostly dated from the period 1940-1955. The major reason for the paucity of information on soybean oil is the diversity of its composition, which depends upon climate and variety; therefore, there is a lack of constancy to more than about three significant figures from sample to sample. Furthermore, the presence of the many minor constituents will be reflected in the differences in many of the properties of crude as compared to refined soybean oil. Partial hydrogenation of soybean oil has a marked effect on the fatty acid composition, so that physical properties are again changed to a significant degree.

For general reviews on physical properties, Jefferson (1950) and Swern (1964) should be consulted.

DENSITY

In addition to the expected dependence upon temperature, the densities of vegetable oils have an inverse relationship with molecular weight and a direct one with the degree of unsaturation. Illustrating the dependence on the latter two variables, an equation has been developed to express the specific gravity of vegetable oils in general (Lund, 1922):

Specific gravity = $0.8475 + 0.00030(\text{Saponification value}) + 0.00014(\text{Iodine Value})$. Saponification values and iodine values can be determined according to Methods Cd 3-25 and Cd 1-25, respectively, according to the Official and Tentative Methods of the American Oil Chemists' Society (AOCS, 1974).

TABLE 1
Density of Soybean Oil at Several Temperatures

Temperature	Density, g/mL	
	Magne and Skau (1945) ^a	Johnstone et al. (1940) ^b
-10.0	0.9410	---
0.0	0.9347	---
10.0	0.9276	---
25.0	0.9175	0.9171
37.8	---	0.9087
40.0	0.9075	---
50.0	---	0.9004

^a Commercial, edible soybean oil having an iodine value of 132.6 and containing 0.10% free fatty acid.

^b Soybean oil that had been refined, bleached, and deodorized and that had the following characteristics: iodine value, 130.1; peroxide number, 5.1; acid number, 0.11; thio-cyanogen number, 80.0; and phosphorus content, 0.00095%.

The densities at several temperatures for soybean oil specifically are given in Table 1.

Of considerable practical value are the densities of soybean oil-solvent mixtures (Magne and Skau, 1945).

A general density equation for glyceride oil-solvent mixtures has been developed (Skau et al., 1955a; 1955b):

$$V = 1/D = a - (a - b + 4k)x + 4kx^2$$

where V = specific volume of oil-solvent mixture, D = density of oil-solvent mixture, a = specific volume of solvent, b = specific volume of oil, x = weight fraction of oil in mixture, $k = \Delta V$ when $x = 0.5$, $\Delta V = V_i - V$, V_i = calculated specific volume of mixture, assuming ideal solutions. For commercial hexane, the value of k can be considered identical for fish and vegetable oils, including soybean, linseed, tung oils: soybean, linseed, tung oils:

Temperature, °C	k , mL/g
10	0.0062
25	0.0080
40	0.0098

The k values have been given for many other solvents including diethyl ether, acetone, heptane, and cyclohexane (Skau et al., 1955a). The k values may also be calculated from exact measurements of solution density at $x = 0.5$ and the known or measured densities of the pure oil and solvent.

The value of such equations lies not only in the convenience for calculating solution densities but also in the ability to calculate composition of solutions from the measured density.

TABLE 2
Refractive Index of Molecularly Distilled Soybean Oil
Fractions of Different Iodine Values^a

Fraction no.	Iodine value	Refractive Index, n_D^{25}		
		Observed	Calculated ^b	Difference ^b
10	128.4	1.4728	1.4726	+0.0002
15	130.2	1.4728	1.4728	0.0000
20	133.2	1.4732	1.4732	0.0000
25	137.5	1.4738	1.4737	+0.0001
30	138.4	1.4740	1.4738	+0.0002

^a Detwiler et al., 1943.

^b Determined for this chapter.

REFRACTIVE INDEX

The refractive indices of liquid fats have a direct relationship to molecular weight (and fatty acid chain length), to degree of unsaturation, and particularly to degree of conjugation, but they have an inverse relation to temperature. The refractive indices of glycerides are considerably higher than those of the individual component fatty acids.

An equation relating refractive index to iodine value has been proposed (Zeleny and Coleman, 1937; Zeleny and Neustadt, 1940):

$$n_D^{25} = 1.45765 + 0.0001164 (\text{Iodine Value})$$

Detwiler et al. (1943) have reported refractive indices for a series of fractions obtained by molecular distillation of crude soybean oil. For the fractions relatively free of unsaponifiables, free fatty acid, and phosphorus, there was good correspondence between the observed refractive index and that calculated from the above equation over the iodine value (IV) range of 128 to 138 (Table 2). The calculations, never off by more than 0.0002 units, indicate the reliability of the equation at least for the range in iodine value indicated.

Johnstone et al. (1940) report the refractive index, $n_D^{25} = 1.4733$, for a refined, bleached, and deodorized soybean oil having an iodine value of 130.1, but this is a discrepancy of 0.0005 from the 1.4728 value calculated by the equation.

Majors and Milner (1938) developed a reverse relationship for estimating the iodine value of crude soybean oil when the refractive index is known:

$$\text{IV} = 8661.723(n_D^{25}) - 12,626.174$$

$$[\text{or } n_D^{25} = 1.45770 + 0.0001154(\text{IV})]$$

Such a relationship depended upon the age of the soybeans, the crop year, and the method of oil recovery (cold pressed or extracted). Within these limitations, the equation (derived from least squares analysis of 270 samples of extracted oil) was quite accurate, giving 0.8 IV units as the standard error. For example, a soybean oil sample having $n_D^{25} = 1.4728$ should have an iodine value of about 130.8 (cf. the value of 130.2 from Table 2).

A similar relationship for refractive index at 40°C has been developed for highly unsaturated oils from several plant families (Cruciferae, Euphorbiaceae, and Labiatae) (Earle et al., 1960):

$$IV = 8555.559(n_D^{40}) - 12,425.928$$

$$[\text{or } n_D^{40} = 1.45238 + 0.0001169 (IV)]$$

Refractive indices for many fats and partially hydrogenated oils are necessarily determined at 40°C, since the fat or oil may be partially solid at 25°C. In order to estimate the refractive index of an oil at a temperature other than the temperature used for the measurement, the following equation from Method Cc 7-25 of the Official and Tentative Methods of the American Oil Chemists' Society can be used (AOCS, 1974)

$$n_D^{t'} = n_D^t + 0.000385 (t - t')$$

where t is the temperature in °C at which the experimental determination was made and t' is the temperature for which an estimate of the refractive index is needed.

Tels et al. (1958) assumed additivity of various atomic and group refractions to calculate the Lorenz-Lorentz molar refraction of fatty acid esters including glycerides, and they developed a relation for the iodine value, saponification value, and specific refraction of fatty oils:

$$r_D^{20} = [(n^2 - 1)/(n^2 + 2)] \times 1/d =$$

$$0.3307 + 1.68 \times 10^{-5} (IV) - 1.41 \times 10^{-4} (SV)$$

where r = specific refraction, n = refractive index (at 20°C), d = density, IV = iodine value, and SV = saponification value. For soybean oil having a saponification value of 192 and an iodine value of 126, a good comparison was obtained for the specific refraction between observed and calculated values:

	r_D^{20}
Observed	0.3054
Calculated	0.3057

The refractive index of soybean oil varies with the wavelength of the light, from 1.4705 (25°C) at 650 nm to 1.5026 (25°C) at 340 nm (Notarnicola, 1974). This dispersion can be expressed by the equation:

$$n^2 = 1 + A\lambda^2/(\lambda^2 - \lambda_0^2)$$

where n = refractive index, A = a constant (1.1307 for soybean oil), λ = the wavelength of the light used, and $\lambda_0 = 11.51504 \times 10^{-11} \text{ cm}^2$.

VISCOSITY

Knowledge on viscosities of soybean oil in solution as well as of the oil itself is essential for design calculations on pumps, piping, and heat transfer equipment. Although viscosity is dependent upon composition, apparently no relationships have been established so that an equation can be developed.

Magne and Skau (1945) have reported viscosities for soybean oil and for its solution in hexane for six different temperatures (-20°C and -10°C in addition to those given in Table 3). Their values agree well with those given by Johnstone et al. (1940) after recalculation of the latter's results.

An inverse relationship between viscosity and unsaturation is implied in the following data from Detwiler et al. (1943):

<u>Iodine value</u>	<u>Viscosity at 25°C, centipoises</u>
128.6	51.7
130.2	50.1
132.5	49.1
136.2	48.2
138.4	48.6

Viscosities of soybean as well as other vegetable oils have been measured recently over a 20 to 160°C temperature range at 10° intervals (Interesse and D'Avella, 1974).

The dynamic shear viscosity at 10-150 MHz and the longitudinal ultrasonic absorption at 50kHz-1000 MHz have been determined for soybean oil (Mikhailov et al., 1975). Volume and shear viscosities had single relaxations, but the volume relaxation time was 10 times larger than the shear. Shear relaxation is apparently the result of molecular orientation, but volume relaxation is the result of rearrangement of molecular packing.

TABLE 3
Viscosity of Refined Soybean Oil^a-Hexane Solutions^b

Hexane ^c , wt%	Viscosity, centipoises			
	0°C	10°C	25°C	40°C
0.00	172.9	99.7	50.09	28.86
11.45	49.03	31.78	18.61	11.95
20.69	21.88	15.40	9.88	6.68
30.80	10.34	7.83	5.43	3.81
39.96	5.69	4.48	3.26	2.44
50.79	3.15	2.57	1.97	1.52
59.70	2.04	1.70	1.34	1.12
78.39	0.91	0.80	0.67	0.56
84.56	0.72	0.64	0.54	0.46

^a Iodine value = 132.6.

^b Magne and Skau, 1945.

^c Skellysolve B.

MELTING POINT

The melting point of a triglyceride depends to a large extent upon those of the component fatty acids, for which melting points increase with increasing chain length, decrease with increasing concentrations of cis double bond configuration, but rise to an intermediate value for increasing concentrations of trans unsaturation (Bailey, 1950). For the octadecenoic acid series, melting points are also dependent upon the position of the double bond and rise as the double bond approaches either end of the molecule (Gunstone, 1973). In the saturated fatty acid series, the triglyceride melts above the fatty acid; in the unsaturated series, the triglyceride melts slightly below (Table 4).

An unsymmetrical triglyceride of the type A-B-A (where B = A + 2 carbons) has a melting point that is a function of total chain length and tends to have a melting point intermediate between those of the highest and lowest melting symmetrical triglycerides. This effect does not hold true for other types of glycerides. Of course, mixtures of triglycerides, as in soybean and other vegetable oils, have depressed melting points compared to that for a homogeneous triglyceride. Finally, one of the major factors in the melting points of triglycerides is polymorphism; the two highest melting and most stable forms for some triglycerides are given in Table 4 to illustrate this point.

Soybean oil, like other fats, requires a lower temperature for solidification than for melting, the difference being only a few degrees when a barely melted oil is cooled again. The solidification point for soybean oil is 3 to 14°F (-16 to -10°C). Differential thermal analysis of soybean oil showed a solidification point at 14°F (-10°C) for a nonstabil-

TABLE 4
Melting Points of Fatty Acids and Their Triglycerides
Present in Soybean Oil and Partially Hydrogenated
Soybean Oils^a

Fatty acid		Triglyceride		
Name	M.p., °C	Name or composition	Melting point, °C	
			I (β)	II (β')
Palmitic	62.9	Tripalmitin	65.5	56.0
Stearic	69.6	Tristearin	73.0	65.0
		18:0-16:0-16:0	62.5	59.5
		16:0-18:0-16:0	68	65
		18:0-16:0-18:0	68	64
Oleic	16.3	Triolein	5.5	-12
		16:0-18:1-16:0	35.2	30.4
		18:0-18:1-18:0	41.6	37.6
		16:0-18:1-18:1	19.0	---
		18:0-18:1-18:1	23.5	---
Elaidic	43.7	Trielaidin	42	37
Linoleic	-6.5	Trilinolein	-13.1	---
Linolenic	-12.8	Trilinolenin	-24.2	---

^a Bailey, 1950.

ized (rapidly cooled) oil and 1°F (-17°C) for a stabilized [slowly cooled to -94°F (-70°C) over a 2-day period] oil (Hannewijk and Haighton, 1958).

As the degree of hydrogenation of soybean oil increases, the melting as well as the solidification point also increases. The increase can be ascribed to reduction in concentration of low melting unsaturated acids and to an increase in the higher melting stearic acid and, in part, to an increase in the trans acids. A fully hydrogenated soybean oil can be expected to have a melting point no higher than about 154°F (68°C), i.e., at a temperature intermediate between tripalmitin (150°F, 65.5°C) and tristearin (163°F, 73.0°C) melting points. The melting points of partially hydrogenated soybean oils have been examined by open-tube (Imamura et al., 1969), Wiley, and automatic dropping point (Doeden, 1975) methods. There is a linear correlation between the latter two methods.

THERMAL PROPERTIES

SPECIFIC HEAT

The specific heat of soybean (Table 5) and other vegetable oils varies directly with chain length and temperature but inversely with degree of unsaturation (Swern, 1964).

The specific heat of hydrogenated soybean oil apparently has not been reported.

HEAT OF COMBUSTION

Bertram (1946) has given a general equation for the heat

TABLE 5
Specific Heats for Soybean Oil With an Iodine
Value of 128.3^a

Temperature		Specific heat, cal./g/°C
°C	°F	
1.2	34.2	0.448
19.7	67.5	0.458
38.6	101.5	0.469
60.9	141.6	0.479
70.5	158.9	0.490
80.4	176.7	0.493
90.4	194.7	0.504
100.4	212.7	0.508
120.8	249.4	0.527
141.3	286.4	0.531
161.9	323.4	0.550
182.7	360.9	0.567
200.1	393.6	0.594
250.5	483.8	0.621

^a Clark et al., 1946.

of combustion of vegetable oils as a function of iodine value and saponification value as follows:

$$-\Delta H_c, \text{ cal/g} = 11,380 - (\text{IV}) - 9.15 (\text{SV})$$

Thus, the calculated value for a soybean oil having an IV of 131.6 and a saponification value of 193.5 is 9,478 cal/g or 16,900 BTU/lb.

An approximate comparison to the energy expenditure in producing 1 lb of soybean oil can be made on the basis that an average bushel of soybeans contains 10.7 lb of crude oil and 47.5 lb of meal. With the assumption that the energy costs can be shared between the meal and oil on a weight basis, the following breakdown can be made:

	BTU/lb of soybean oil
Soybean production, net energy cost	1755
Soybean crushing, net energy cost	1032
Refining costs for producing cooking oil	2400
Total	5187

Should the necessity arise, soybean oil can be used as a fuel, since its energy content is higher than the energy expended in its production. Indeed, soybean oil can be burned

TABLE 6
Smoke, Flash, and Fire Points of Soybean Oil^a

Soybean Oil		Smoke point, °F (°C)	Flash point, °F (°C)	Fire point, °F (°C)
Description	Free fatty acid content, %			
Refined and bleached	0.010	453 (234)	623 (328)	685 (363)
Refined and bleached	0.010	443 (228)	625 (329)	685 (363)
Crude, expeller pressed	0.51	365 (185)	565 (296)	660 (349)

^a Morgan, 1942.

in a diesel engine by itself or in mixture with diesel fuel. Depending on the use, crude, degummed, or refined soybean oil can be used as a fuel.

SMOKE, FLASH, AND FIRE POINTS

These properties to a major extent are functions of the free fatty acid content in soybean oil, the fatty acids being much more volatile than the glyceride (Swern, 1964). The temperatures for these characteristics are generally similar for all vegetable oils having comparable fatty acid composition and low free fatty acid content. The temperatures are lower for the lauric acid-containing oils such as coconut oil even if the content of free fatty acids is low. The temperatures for smoke, flash, and fire points of soybean oil are given in Table 6.

These physical characteristics are improved when cottonseed and peanut oils are bleached, apparently as the result of removal of an unknown impurity (Morgan, 1942). The impurity or impurities can also be removed by steam stripping and by alkali refining. Presumably, the same effects will take place with soybean oil.

The practical aspects of these characteristics as far as the consumer is concerned have been discussed in an article in Consumer Reports (Anonymous, 1978). Ratings based on smoke points are given for 37 consumer-available cooking oils.

SOLUBILITY

GENERAL

Soybean oil is miscible with many organic solvents, particularly those that are apolar and aprotic, i.e., those that do not form hydrogen bonds. Hydrocarbons, esters, ethers, ketones, and chlorinated solvents are among those

solvents having miscibility with soybean oil. Ethanol, isopropyl, and isobutyl alcohols, ethylene dichloride, trichloroethylene, carbon tetrachloride, and hexane have been examined in the laboratory as extraction solvents (Beckel et al., 1948). Ethanol extraction reportedly gave the best results with respect to oil color, meal, and protein as well as meal flavor and color.

In order to have miscibility, the polarities of the oil and the solvent should be of the same order of magnitude. Accordingly, solubility characteristics can be roughly estimated from a knowledge of dielectric constants or solubility parameters as a measure of polarity (Table 7).

HYDROCARBONS

Propane has been used in a pilot process for either fractionation or refining of animal or vegetable oil (Passino, 1949), but the process did not reach commercial status for soybean oil. The low boiling point of propane (-43.8°F, -42.1°C) requires that the process be carried out under pressure--about 400 psig. At about room temperature the oil is miscible, but as the temperature is raised, solubility is reduced until the critical point (206°F, 96.7°C) is reached. In fractionating soybean oil, the following cuts were obtained:

I (color cut)	2%
II (IV = 155)	25%
III (IV = 128)	72%
IV	1%

Cut IV contained most of the free fatty acids and the unsaponifiables. Cut II is an improved drying oil, and Cut III is suitable for edible products. In a straight refining operation, a 2% color body fraction was removed, and the deodorization step was then used to remove free fatty acids.

Hexane is the preferred solvent for commercial extraction of oil from soybean flakes (see Chapter 4. Recovery of Oil from Soybeans), although methylpentane was found to be more efficient and to give better colored oils in laboratory tests with cottonseed (Ayers and Scott, 1951).

FURFURAL

For several years during World War II and the post-war period, furfural was used to fractionate nonbreak soybean oil on a commercial scale to produce an improved drying oil because of shortages of linseed oil for paints. Furfural and soybean are not miscible at normal temperatures, and their

TABLE 7
Dielectric Constants and Solubility Parameters^a
of Solvents vs. Vegetable Oils

Solvent	Dielectric constant	Solubility parameter ^b
Water	78.5	23.53
Furfural	41.9	10.09
Methanol	32.6	14.50
Ethanol	24.3	12.78
1-Propanol	20.1	12.18
2-Propanol	18.3	11.44
Acetone	21.4	9.62
Sulfur dioxide	14.1	---
Trichloroethylene	3.4	9.16
Vegetable oils	3.0-3.2	---
Cyclohexane	2.05	8.19
Hexane	1.89	7.27
2-Methylpentane	---	7.03
Propane	1.61	5.77
Carbon dioxide	1.60	---

^a Hoy, 1970.

^b Solubility parameter, δ , is defined as follows:

$$\delta = (\Delta E/V)^{1/2} = [(\Delta H - P\Delta V)/V]^{1/2}$$

mixtures separate into two phases (Gloyer, 1948; 1950). The solvent-predominant phase contains the more unsaturated glycerides, whereas the oil-predominant fraction contains the more saturated glycerides. Thus, with a 14:1 solvent:oil ratio, the extract contained 70% of the oil (IV = 153.2) and the raffinate contained 30% of the oil (IV = 95.5). Furfural in combination with naphtha in a 2-column system could be used to refine crude or degummed soybean oil. An intermediate oil fraction recovered from the first column had an IV of 109, contained 0.05% free fatty acids, and amounted to 39% of the original oil. A light-colored, break-free, varnish-type oil (IV = 152.3) having a relatively low free fatty acid content (0.15%) was recovered in the second column by naphtha stripping of the furfural phase. A 1% byproduct fraction recovered from the stripped furfural contained 17% of free fatty acids and 7.8% of unsaponifiables.

CHLORINATED SOLVENTS

Chlorinated solvents such as trichloroethylene and ethylene dichloride dissolve soybean oil completely, but use of these solvents causes toxic materials to form in the meal (see Chapter 4. Recovery of Oil from Soybeans). Physical properties for solutions of soybean oil in these chlorinated solvents as well as in hexane have been reported by Johnstone et al. (1940).

ACETONE

Acetone and methyl acetate are miscible with soybean oil; but at low temperatures the more saturated glycerides crystallize, leaving the more unsaturated glycerides in solution (Bull and Wheeler, 1943). For example, at -40°C and a solvent-to-oil ratio of 10:1 (vol:wt), a 41% yield of oil with IV = 150.7 and a 59% yield of oil with IV = 119.4 were obtained. Addition of 1% water to the acetone raised the temperature at which comparable results were obtained, but a greater solvent ratio was required.

ALCOHOLS

Ethanol, anhydrous as well as aqueous, is not a good solvent for soybean oil at normal temperatures, but as the temperature increases, the solubility increases until the critical solution temperature is reached, at which point the components become miscible (Table 8) (Rao et al., 1955; 1957). At about 86°F (30°C), solubility of soybean oil in aqueous or anhydrous ethanol is no more than 3-6%. Pressures of about 20 psig are required for extraction of the oil from soybeans with practical quantities of these solvents. Isopropyl alcohol (2-propanol) is a better solvent (Table 8) (Rao and Arnold, 1957); somewhat lower pressures are required than for ethanol.

Methanol is a poor solvent because of its polarity (a dielectric constant of 32.6 compared to 24.3 for ethanol).

SULFUR DIOXIDE

Solubility of soybean oil in liquid sulfur dioxide apparently has not been reported, but Schlenk and Ener (1959) give the following solubilities of triglycerides:

triolein (-17°C)	350 mg/100 g
triolein (-27°C)	27 mg/100 g
trilinolenin (-13)	1.25 g/100 g

These authors state that unsaturated lipids are obtained as yellow oils that are difficult to decolorize by vacuum.

SOLUBILITY OF OXYGEN IN SOYBEAN OIL

The solubility of oxygen at room temperature ($22-23^{\circ}\text{C}$) as measured by an exponential dilution method varies from 1.3 ml/100 ml of refined oil to 3.2 ml/100 ml of crude soybean oil, with the respective coefficients of solubility of 0.070

TABLE 8
Critical Solution Temperatures for Miscibility of
Crude Soybean Oil in Aqueous Ethanol and 2-Propanol^a

Concentration of aqueous alcohol ^b	Critical solution temperature, $^{\circ}\text{C}$	
	Ethanol	2-Propanol
wt %		
99.9	67	(miscible)
98.0	78	35
95.4	90	45
91.5	--	70

^a Rao et al., 1955; 1957.

^b Before mixing with soybean oil.

TABLE 9
Representative Values for Selected
Physical Properties of Soybean Oil

Property	Value
Specific gravity, 25°C	0.9175 ^a
Refractive index, n_D^{25}	1.4728 ^b
Specific refraction, r_D^{20}	0.3054
Viscosity, centipoises @ 25°C	50.09 ^a
Solidification point, $^{\circ}\text{C}$	-10 to -16°C
Specific heat, cal/g @ 19.7°C	0.458
Heat of combustion, cal/g	9,478 ^c
Smoke point, $^{\circ}\text{F}$ ($^{\circ}\text{C}$)	453 (234)
Flash point, $^{\circ}\text{F}$ ($^{\circ}\text{C}$)	623 (328)
Fire point, $^{\circ}\text{F}$ ($^{\circ}\text{C}$)	685 (363)

^a IV = 132.6.

^b IV = 130.2.

^c IV = 131.6.

nd 0.173 (Aho and Wahlroos, 1967).'

SUMMARY

Some of the more important physical properties of soybean oil are summarized in Table 9; the values are representative and not absolute, because the composition of soybean oil and many of the properties depend upon degree of unsaturation and other factors.

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